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ELECTROLYTIC PREPARATION OF HIGH DIELECTRIC FILMS

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Section 1

INTRODUCTION

The objective of this investigation is the preparation of high dielectric materials in thin film form on refractory metal substrates by electrochemical techniques. Work performed during this quarter has been directed toward forming titanate, zirconate, niobate, and tantalate films. The baths used have been of the EDTA type previously described and have used Group IIA cations as complexed potential film modifiers. Heat treatment of the films in air and in vacuum to improve the electrical characteristics has been initiated. The presence of the modifying cations of barium and calcium in the film has been corroborated.

Section 2

FILM PREPARATION AND COMPOSITION

2.1 GENERAL PROCEDURE

A detailed description of substrate preparation and film formation can be found in the earlier progress reports. The EDTA bath is made by mixing a solution of boric acid, potassium hydroxide and the sodium salt of ethylenediaminetetracetic acid with a solution of the metal acetate. Baths prepared in this manner do not immediately precipitate, although standing for long times the solution will sometimes become cloudy. The baths used in this quarter's study are shown in Table 1. They will be referred to in the presentation of data concerning the films and will simply be labeled according to the metal acetate complexed. If data concerning films made in a different bath than those listed are presented, then the bath composition will be indicated. Actually, baths can be made using magnesium, tin, lead and probably any metal whose acetate is soluble and is not in Group I of the periodic chart.

TABLE I
Composition of EDTA-Me Acetate Baths

<u>Bath Name</u>	Concentration g/l				<u>pH</u>
	<u>H₃BO₃</u>	<u>KOH</u>	<u>NaEDTA</u>	<u>Metal Acetate</u>	
Barium	6.6	13.2	39.0	31.5	9
Calcium	6.6	13.2	39.0	10.8	9
Strontium	6.6	13.2	39.0	26.5	9
Barium-Strontium	6.6	13.2	39.0	22, 8.0	9

2.2 STRIPPING OF FILMS

Analysis of the film composition has been made by semiquantitative spectrographic methods. These analyses have been performed on the films after being removed or stripped from the substrate. The technique used is only one of several available for titanium and consists of scratching the film with a razor blade or other knife edge to expose some fresh metal. The piece is then placed in a 2.5 to 5% solution of bromine in dry methanol. After about 24 hours the titanium and zirconium substrates have been dissolved leaving the film. Niobium is only very slightly attacked by this reagent and tantalum is not attacked at all. Several other techniques including an HgCl_2 method have been tried, but none have been satisfactory for tantalum or niobium. A technique of heating niobate films formed in these baths to 300°C results in the film lifting off the substrate very cleanly. Analysis of films stripped in this manner have not been completed. Tantalum treated in the same manner does not react in the same way.

2.3 COMPOSITION OF FILMS FORMED IN EDTA BATHS

The semiquantitative spectrographic analysis of films formed on titanium and zirconium are shown in Table 2. Although partial stripping of film on niobium was achieved, sample size was insufficient and the analytical results were less than satisfactory. All samples were prepared by anodizing at 100 ma/cm_2 for two minutes at bath temperatures of 25 to 35°C . The results are listed for two separate samples on each substrate in each bath. The results enclosed by paranthesis were reported on only one of the samples. Otherwise the reported metals were found in the same classification in both samples. A second experiment was made in which titanium and zirconium were anodized for five

TABLE 2
Spectrographic Analysis of Films
Formation Time 2 Minutes

<u>Substrate</u>	<u>Bath Used</u>	<u>Elemental Composition</u>		
		<u>Major >10%</u>	<u>Minor 1%-10%</u>	<u>Trace <1%</u>
Titanium	Barium	Titanium		Barium, Iron Silicon
	Calcium	Titanium Calcium		
	Strontium	Titanium		
	Barium Strontium	Titanium Barium		(Nickel)
Zirconium	Barium	Zirconium		Barium Silicon
	Calcium	Zirconium Calcium		
	Strontium	Zirconium		
	Barium Strontium	Zirconium Barium		Nickel Nickel
Niobium	Barium	Niobium Barium	Silicon	
	Calcium	Niobium Calcium		titanium

minutes in a barium bath. The spectrographic analysis revealed major amounts of the barium with the substrate metal, minor amounts of calcium and traces of nickel.

These results indicate that major amounts of Group II metals can be occluded in an anodic film on titanium zirconium and niobium. It also shows that the concentration of barium in the film is a function of the anodization time. The

absence of strontium in the film is noteworthy. At the pH of the bath, the Group II metal should precipitate if it is not complexed. The strontium bath was cloudy in appearance even when freshly made indicating that the complex is not being formed. Without the complex it is impossible to get the desired metal to the anode. These new results collaborate earlier data reporting the presence of barium in the titanium anodic film.

2.4 X-RAY ANALYSIS

Samples of the zirconium films prepared in a calcium acetate bath were analyzed by x-ray diffraction. The bath used was slightly different than those described in Section 2.1 in that the calcium acetate concentration was about 22 g./liter. One sample was heated in air for one hour at 500°C. The data is shown in Table 3. Both the heat-treated and as-produced samples are crystalline and are a mixture of the monoclinic, cubic and tetragonal forms. Heat treatment causes a few lines to disappear and some new ones to appear.

TABLE 3

X-Ray Data Zirconium Anodic Films

Intensity Code: S = Strong, M = Medium, W = Weak, VW = Very Weak

As Prepared		Heat Treated 500°C 1 Hour		Baddeleyite Monoclinic		Tetragonal		Cubic	
d	Intensity	d	Intensity	d	I/I ₀	d	I/I ₀	d	I/I ₀
				5.05	5				
4.10	VW			3.69	15				
3.62	W	3.62	W	3.63	12				
3.15	M	3.15	M	3.16	100				
2.93	S	2.93	S			2.92	100	2.93	100
2.80	M	2.80	M	2.84	65				
				2.62	20				
				2.60	12				
2.55	M	2.55	M	2.54	15	2.52	40	2.53	60

d	Intensity	d	Intensity	d	I/I ₀	d	I/I ₀	d	I/I ₀
2.32	W			2.50	3				
				2.33	5				
		2.20	W	2.21	10				
				2.19	5				
2.18	W			2.18	5				
		2.00	W	2.02	7				
				1.990	7				
				1.846	15				
				1.817	20	1.81	60		
1.80	S	1.80	S	1.802	12			1.80	100
				1.781	5	1.79	100		
		1.68	VW	1.693	10				
				1.655	12				
1.64	W	1.64	W	1.642	7				
				1.609	5				
				1.591	5				
				1.581	5				
						1.55	50		
1.54	S	1.54	M	1.542	10	1.53	100	1.53	100
				1.508	5				
				1.495	5				
1.47	M	1.47	W	1.477	10	1.47	60	1.464	30
				1.449	3				
1.42	VW	1.41	W	1.420	7				
				1.360	2				
				1.32	5				
						1.29	40		
1.275	VW	1.28	VW	1.262	5	1.27	60	1.267	30
				1.246	2				
				1.213	2				
						1.17	40		
1.175	M	1.17	M			1.16	70	1.164	30
						1.13	40	1.133	30
1.143	M	1.14	W			1.10	60		
						1.05	40		
1.045	M	1.04	M			1.04	70	1.035	30
0.985	M	0.985	W			0.993	40		
						0.978	70	0.967	30
0.905	VW								
								0.8968	20
0.865	M	0.866	W						
0.853	VW	0.853	W					0.8575	30
								0.845	20
								0.802	20

SECTION 3

ELECTRICAL PROPERTIES

3.1 INTRODUCTION

The electrical properties of capacitance, dissipation factor, and resistance have been measured for the electrochemical conversion films. The reproducibility, effect of bath type, and anodization time have been determined using as-produced films. A study of the effect of heat treatment on the films electrical properties has been initiated during this quarter. Film thicknesses have been taken which can be used to calculate an effective dielectric constant.

3.2 REPRODUCIBILITY OF CAPACITANCE

In the remaining contract period, much of the effort will be directed toward developing processing steps that will improve the dielectric constant of the films. The major criteria to be used in evaluating films will be the capacitance using a Ag carbon counter electrode. In order to evaluate the data, it is necessary to know the spread of values that might be obtained from a bath. To establish this range, a series of nine samples on titanium substrates from the same barium bath were run at the same conditions, namely 100 ma/cm² current density for five minutes at 22 to 30°C. Four counter electrodes were painted on the sample and the capacitance measured. The data is presented in Table 4. Three of the nine samples consistently average about 1/2 the average of the other six. Agreement between capacitance values obtained from the electrodes on any one sample is quite good. Inspection of the formation data has failed to disclose the reason for the low capacitances of these three samples. The possible influence of film composition will be examined during the next quarter. However, this information will be useful in evaluating the data obtained in other studies.

TABLE 4

Reproducibility of Capacitance Values

Anodizing Conditions:	100 ma/cm ²	current density
	22 - 30°C	bath temp.
	5 min.	anodizing time
	barium	bath type
	titanium	substrate

Values are nf/cm²

Sample 11 - 85 -

Electrode	A	B	C	D	E	F	G	H	I
1	25.0	20.1	26.9	9.3	9.8	19.3	22.8	17.6	9.6
2	17.6	16.7	14.2	7.4	9.8	18.1	19.8	19.9	
3	19.6	19.1	21.6	8.1	10.5	14.7	24.5	20.1	8.8
4	19.3	19.1	18.6		8.6		21.3	18.6	
Average	20.4	18.1	20.3	8.3	9.7	17.4	22.1	19.0	9.2

3.3 THE EFFECT OF BATH TYPE AND ANODIZATION TIME

A comparison of capacitance values for films produced in the four bath types is shown in Table 5. Allowing for the slight differences in preparation noted in the data, the values from all baths on any particular substrate are identical. The presence of barium, calcium, or probable absence in the case of samples prepared in the strontium bath does not influence the capacitance in unfired films.

The effect of anodization time on the capacitance and thickness of the film is shown in Table 6. In this one study, only tantalum was used as the substrate. As can be seen the capacitance decreases and the film thickness increases with anodization time.

TABLE 5

Effect of Bath Type

Substrate	Bath Type	Current Density ma/cm ²	Time Min.	Temp. °C	Final		Capacitance nf/cm ²	Dissipation Factor	Thickness Microns
					Volts	Volts			
Titanium	Barium	100	5	22-37	230	8.3 to 22.1	0.11 to 0.34	3	
	Calcium	100	5	23-34	250	8.1	0.13	5	
	Strontium	100	5	25-29	250	5.9	0.08		
	Barium Strontium	100	2	26-32	200	22.6	0.14		
Zirconium	Barium	100	1	26-28	280	5.4	0.026		
	Calcium	100	2	24-29	320	3.5	.025		
	Strontium	100	2	26-35	310	3.3	.036		
	Barium Strontium	100	2	23-30	300	3.9	0.028		
Niobium	Barium	100	2	36-24	250	9.3	0.12	6	
	Calcium	100	2	32-27	260	6.9	0.062	8	
	Strontium	100	2	21-27	260	6.0	0.045	10	
	Barium Strontium	100	2	24-28	260	6.15	0.057	9	
Tantalum	Barium	100	2	24-30	290	12.5	0.082	4	
	Calcium	100	2	24-27	290	9.8	0.125	4	
	Strontium	100	2	21-27	300	15.8	0.076	5.6	
	Barium Strontium	100	2	24-28	290	10.5	0.10	4	

TABLE 6

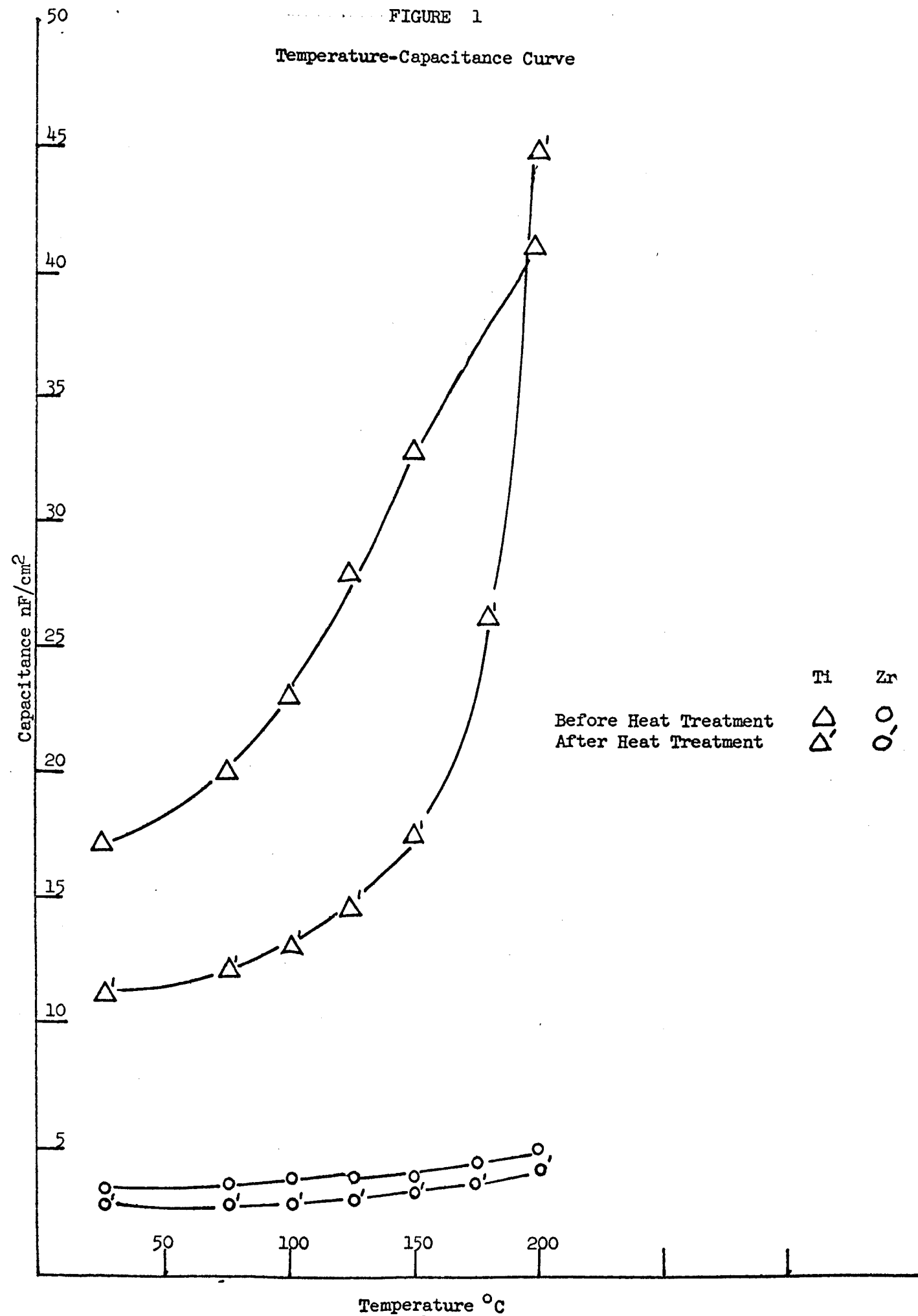
Effect of Anodization time

Bath Type	Anodization Time - Min.	Capacitance nf/cm^2	Dissipation Factor	Thickness Microns
Barium	2	8.6	0.073	6.6
	4	5.3	0.082	13.
	5	4.2	0.071	13.5
Calcium	2	9.1	0.085	6
	4	5.4	0.058	9
	5	4.9	0.069	13.5
Strontium	2	15.4	0.040	4.5
	4	7.8	.043	8
	5	4.1	.047	18
Barium	2	8.8	0.10	6.5
Strontium	4	4.6	0.085	12
	5	2.9	0.061	15

3.4 HEAT TREATMENT OF FILMS IN AIR

Samples of titanium and zirconium were anodized in the four baths at 100 ma/cm^2 for one minute or 200 ma/cm^2 for 0.5 minute. The capacitance as a function of temperature and electrical resistance of the films was measured. The samples were then placed in an oven at 950°F (510°C) for various lengths of time. The samples were in the air during this heat treatment. The temperature - capacitance curve and the electrical resistance was redetermined. A typical temperature-capacitance curve is shown in Figure 1. As can be seen the heat treatment lowers the capacitance and the temperature coefficient of the capacitance up to about 100°C for the films formed on both titanium and zirconium. These results are typical of films formed on titanium in all baths. Prolonged heat treatment of the zirconium films completely destroys the capacitance

FIGURE 1
Temperature-Capacitance Curve



properties. The dissipation factor is lowered slightly which would be expected with the lowering of the capacitance.

There is no indication of titanate formation due to this heat treatment. The results of the spectrographic analysis of the films indicate that the correct forming conditions may not have been used, and the films had little or no metal deposited from the solution. Additional films will be formed and further data obtained. Some representative resistance (in megohms) before and after heating are shown in Table 7, at several applied voltages. The resistance of the titanate films is changed little if any by this heat treatment while

TABLE 7

		Resistance of Films							
Substrate	Bath	Before Heat Treatment			After 8 Hours Heat Treatment				
		2	4	6	2	60	80	100	
Titanium		1			1				
		10	1	1	20	2	1		
		3	1	1	20	1.5	1		
Zirconium		5×10^4	10^4	1	10^5	10^5	3×10^4	5×10^3	

the zirconium films show large increases in resistance. Measurement of the resistance of the heated metal was made to determine if the large resistance could be attributed to the substrate. The results showed this to be true. Thus, the anodic film is probably conductive to some degree. It is not feasible to perform heat treatments in air at any higher temperatures due to excessive oxidation of the metal. The air heat treatment can possibly be used as a final step in a series of heat treatments in which a reduced oxide film is obtained.

3.5 VACUUM HEAT TREATMENT

Initial experiments in vacuum heat-treating of the films have been carried out. It was anticipated that films would be reduced due to reaction of the metal substrate with the oxide. The films may be healed by a second heat treatment at a lower temperature in air. In the first experiments films prepared on tantalum, titanium, and niobium were placed in quartz ampules and evacuated to about 5μ Hg and sealed. They were heat treated at 800°C for two hours. The films were prepared in the strontium and barium strontium baths.

The tantalum and niobium films darkened noticeably and the capacitance and dissipation factor were high due to the reduced nature of the oxide. The titanium oxide disappeared due to the high affinity of titanium metal for oxygen at elevated temperature. Subsequent experiments have shown that the titanium can be heat treated at 700°C without destroying the coating.

Heat treating the fired films in air has been attempted. The niobium films flake off if heated at 300°C . A thirty minute treatment of the niobium at 200°C does not affect the capacitance or dissipation factor of the fired films. The tantalum films can be healed by heating at 500°C in air for one hour. Although a few capacitance measurements indicate that some improvement was made, no definite conclusion can be made until more data is obtained.

SECTION 4

FUTURE WORK PLANS

In the final quarter of this contract, emphasis will be placed upon heat treatment of films formed on tantalum, niobium, zirconium, and titanium. Alternate techniques of forming films will be used and the films will be subjected to similar heat treatments. Some experiments in gas anodization are also being designed and will be carried out during the final quarter of the program.